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(54) Addition polymerization catalyst with oxidative activation

Additionspolymerisationskatalysator mit oxidativer Aktivität

Catalyseur de polymérisation, type addition, avec action oxydante

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(73) Proprietor: **THE DOW CHEMICAL COMPANY**
Midland, Michigan 48640 (US)

(72) Inventor: **LaPointe, Robert E.**
Midland, Michigan 48640 (US)

(74) Representative: **Burford, Anthony Frederick et al**
W.H. Beck, Greener & Co.
7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ (GB)

(56) References cited:
EP-A- 0 277 004 **EP-A- 0 418 044**
EP-A- 0 421 659 **EP-A- 0 426 637**

• **J. AM.CHEM.SOC. vol. 109, 1987, pages 4111 - 4113; R.F. JORDAN: 'CHEMISTRY OF CATIONIC ZIRCONIUM(IV) BENZYL COMPLEXES. ONE ELECTRON OXIDATION OF d0 ORGANOMETALLICS.'**

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EP 0 468 651 B1

Description

This invention relates to compositions of matter that are useful as catalysts, to a method for preparing the compositions of these catalysts, and to a method of using the compositions as addition polymerization catalysts. More particularly, this invention relates to catalyst compositions, to a method of preparing these catalyst compositions and to a method for polymerizing olefins, diolefins and/or acetylenically unsaturated monomers wherein these catalysts are used.

The use of Ziegler-Natta type catalysts in the polymerization of addition polymerizable monomers is, of course, well known in the prior art. In general, these soluble systems comprise a Group 4 or Lanthanide metal compound and a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst.

In EP-A-0277,004 there are disclosed certain bis(cyclopentadienyl) metal compounds formed by reacting a bis(cyclopentadienyl) metal complex with salts of Bronsted acids containing a non-coordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in the polymerization of olefins.

Disadvantageously it has now been found that catalysts prepared according to the foregoing technique are detrimentally affected by the presence of by-product amine or phosphine compounds resulting from the catalyst formation. That is, the procedure of EP-A-0277,004 involves an irreversible reaction between a ligand of the metal compound and a cation of the Bronsted acid salt. In practice such cations are generally trialkyl ammonium or phosphonium ions that result in the formation of a tertiary amine or phosphine by proton transfer to the ligand during catalyst formation. Such amine or phosphine compounds are undesirable components of the resulting catalyst due to their inhibiting effect on addition polymerizations.

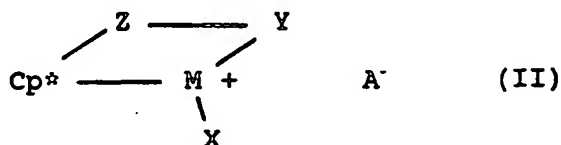
It would be desirable if there were provided a addition polymerization catalyst that is activated in a manner that forms only noninterfering and inert by-products.

In *J. Am. Ch. Soc.* 109, 4111-4113 (1987) there is disclosed a process for preparation of cationic zirconium (IV) benzyl complexes by one electron oxidation of d^0 organometallic compounds. The solvents employed in the preparation of the zirconium metallocenes were tetrahydrofuran or methylene chloride both of which interfere with the desired catalyst formation and or detrimentally affect subsequent olefin polymerizations. In addition the reference employed an oxidizing agent containing tetraphenylborate. Such anions, it has now been discovered, are unacceptable for use in an oxidation activation process for preparing addition polymerization catalysts.

It has now been discovered that the foregoing and other disadvantages of the prior art ionic olefin polymerization catalysts can be avoided or at least reduced with the catalysts of the present invention. In addition an improved catalyst activation procedure and improved addition polymerization processes are provided according to the present invention. It is, therefore, an object of this invention to provide improved ionic catalyst systems which are useful in the polymerization of addition polymerizable monomers including olefins, diolefins and/or acetylenically unsaturated monomers. It is another object of this invention to provide a method for preparing such improved catalysts. It is a further object of this invention to provide an improved polymerization process using such improved catalysts. It is still another object of this invention to provide such an improved catalyst which is not subject to formation of interfering compounds. Finally it is an object of this invention to provide such an improved catalyst which may permit better control of the product polymer molecular weight and molecular weight distribution.

EP-A-0418044 (published 29th January 1992) discloses, inter alia, that the compounds of Formula II infra are novel addition polymerization catalysts. It teaches that said compounds are prepared by analogous processes to those of EP-A-0277044 and hence, in practice, they are contaminated by tertiary amine or phosphine compounds resulting from reaction of the cation of the Bronsted acid reactant with the metallocene reactant.

In accordance with a first aspect of the present invention, there is provided a process for preparing an addition polymerization catalyst of the formula (II):



wherein:-

M is a metal of Group 4 or the Lanthanide series of the Periodic Table of the Elements;

X is hydride or a hydrocarbyl, silyl or germyl group having up to 20 carbon, silicon or germanium atoms;

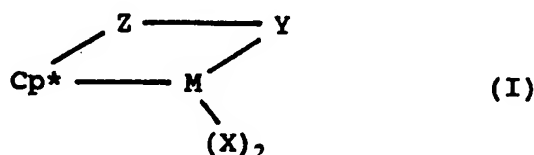
Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound to Z and bound in an η^5 bonding mode to M, said substituents being independently selected from hydrocarbyl radicals, substituted-hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by halogen atoms, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, or halogen radicals or two or more such substituents together form a fused ring system;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system; and

A⁻ is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom selected from aluminum, gold, platinum, boron, phosphorus and silicon,

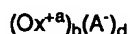
comprising contacting a derivative of a Group 4 or Lanthanide metal corresponding to the formula (I):



wherein:-

M, X, Cp*, Z and Y are as defined above

with an oxidizing agent which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent corresponding to the formula:



wherein:-

Ox^{+a} is a non-Bronsted acid, cationic oxidizer having a charge of (+a) selected from ferrocenium ions, bis-indenyl Fe(III) ions, cationic derivatives of substituted ferrocene, Ag⁺¹, Pd⁺², Pt⁺², Hg⁺², Hg₂⁺², Au⁺ and Cu⁺;

A⁻ is as previously defined; and

b and d are integers selected to provide charge balance.

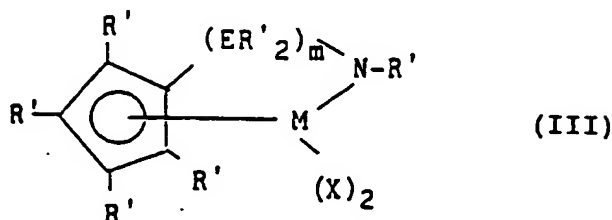
The invention further provides an addition polymerization catalyst of Formula II (as defined above), said catalyst lacking in amine or phosphine byproducts and being obtainable by the process of the invention.

All references to the Periodic Table of the Elements herein refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups is to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Preferably M is a metal of Group 4 of the Periodic table of the Elements, most preferably titanium or zirconium. Also, preferably X is hydride or C₁-C₁₀ hydrocarbyl.

Suitable hydrocarbyl and substituted-hydrocarbyl radicals, which may be substituted for at least one hydrogen atom in the cyclopentadienyl radical Cp*, contain from 1 to 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Suitable organometalloid radicals include mono-, di- and trisubstituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contain from 1 to 20 carbon atoms. More particularly, suitable organometalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, and trimethylgermyl.

The most preferred reactants of Formula I are "amidosilane"- or "amidoalkanediy"- compounds corresponding to the formula (III):



wherein:

M is titanium or zirconium, bound to an η^5 -cyclopentadienyl group;

R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms or two R' together with the cyclopentadienyl group form an indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl ring;

E is silicon or carbon;

X independently each occurrence is hydride, trimethylsilyl, or a moiety selected from alkyl, aryl and combinations thereof of up to 10 carbons; and

m is 1 or 2.

Examples of the above most preferred metal coordination compounds of Formula III include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, or octahydrofluorenyl; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl; and X is methyl, neopentyl, trimethylsilyl, norbornyl, benzyl, methylbenzyl or phenyl. Specific compounds include:

(tert-butylamido)-(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediy/zirconium dimethyl,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediy/titanium dimethylbenzyl,
 (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethane-diy/zirconium dibenzhydryl,
 (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethane-diy/titanium dineopentyl,
 (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)-methylenetitanium diphenyl,
 (tert-butylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl)-silanezirconium dibenzyl,
 (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silanetitanium di(trimethylsilyl),
 (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silanezirconium dibenzyl,
 (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silane dibenzylzirconium,
 (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silane dibutyltitanium, and
 (tert-butylamido)dimethyl(tetraethyl- η^5 -cyclopentadienyl)-silane dibenzyltitanium.

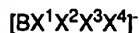
In the most preferred embodiment -Z-Y- is an amidosilane or amidoalkane group of up to 10 nonhydrogen atoms, eg. (tert-butylamido)(dimethylsilyl) and (tert-butylamido)-1-ethane-2-yl.

The cationic oxidizer Ox^{+a} has an oxidation potential sufficient to cause a molecular oxidation of the derivative of a Group 4 or Lanthanide metal so as to form a catalytic species. Generally and preferably the Group 4 or Lanthanide metal of the derivative compound is already in the highest atomic oxidation state. The process of the invention involves a molecular oxidation. Most preferred cationic oxidizers have an oxidation potential of at least +0.20 volt and preferably at least +0.25 volt. Cationic oxidizers are not Bronsted acids.

The anion A^- , when functioning as a charge balancing anion in the catalyst system of this invention does not transfer an anionic substituent or fragment thereof to any cationic species thereby forming a neutral Group 4 or Lanthanide metal product and is not degraded to neutrality during catalyst preparation or use.

Oxidizing agents containing anions comprising a coordination complex containing a single boron atom are most preferred.

Anions comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:

5 B is boron in a valence state of 3;

X^1 to X^4 are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms. In addition two or more of X^1 to X^4 may be linked to each other through a stable bridging group. Preferably X^1 to X^4 lack reactive hydrogen moieties. That is, the radicals are either devoid of hydrogen, contain only hydrogen
10 in nonactivated positions or contain sufficient steric hindrance to protect potentially active hydrogen sites. Examples of suitable radicals for X^1 to X^4 are perfluorinated hydrocarbyl radicals containing from 6 to 20 carbon atoms, 3,4,5-trifluorophenyl and 3,5-bis(trifluoromethyl)phenyl.

A most highly preferred anion is tetra(pentafluorophenyl)borate.

15 Most preferred cationic oxidizers are ferrocenium and Ag^{+1} cations.

Examples of oxidizing agents are ferrocenium tetra(pentafluorophenyl)borate, gold (I) tetrakis (3,4,5-trifluorophenyl)borate, silver tetra(pentafluorophenyl)borate and 1,1'-dimethylferrocenium tetrakis (3,5-bis(trifluoromethyl)phenyl) borate.

Without wishing to be bound by any particular theory of operation it is believed that the cationic oxidizer causes the
20 molecular oxidation of the Group 4 or Lanthanide metal derivative, and in the process becomes a neutral species. The oxidized metal derivative loses a hydrogen or hydrocarbyl radical ($\cdot R$) by a unimolecular elimination reaction. Two or more such radicals form a hydrogen molecule or a neutral organic species of the formula R_x where x is an integer greater than or equal to 2. These byproducts are of course neutral or noninterfering with any subsequent polymerization reaction and may also be removed from the reaction mixture. This result is much preferred to previously known processes for catalyst activation which resulted in the formation of an amine or similar reaction byproduct.

It should be noted that the two compounds combined for preparation of the active catalyst must be selected so as to avoid transfer of a fragment of the anion, particularly an aryl group, to the metal cation, thereby forming a catalytically inactive species. This could be done by steric hindrance, resulting from substitutions on the groups attached to the Group 4 or Lanthanide metal as well as substitutions on the aromatic carbon atoms of the anion. It follows, then, that
30 Group 4 and Lanthanide metal compounds (first components) comprising, for example, perhydrocarbyl-substituted cyclopentadienyl radicals could be effectively used with a broader range of second compounds than could first components comprising less bulky radicals. As the amount and size of the metal substituents are reduced, however, more effective catalysts are obtained with second compounds containing anions which are more resistant to degradation, such as those with substituents on the meta and/or para positions of the phenyl rings. Another means of rendering the
35 anion more resistant to degradation is afforded by fluorine substitution, especially perfluorosubstitution, in the anion. Second components containing fluoro-substituted stabilizing anions may, then, be used with a broader range of first components.

In general, the catalyst can be prepared by combining the two components in a suitable solvent at a temperature within the range from -100°C to 300°C .

40 The catalyst may be used to polymerize α -olefins and/or acetylenically unsaturated monomers having from 2 to 18 carbon atoms and/or diolefins having from 4 to 18 carbon atoms either alone or in combination. The catalyst may also be used to polymerize α -olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers. In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and pressures
45 from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry or other process condition may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous manner. It will, of course, be appreciated that the catalyst system will form *in situ* if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent prior to adding the
50 same to the polymerization mixture.

As indicated supra, the improved catalyst of the present invention will, preferably, be prepared in a suitable solvent or diluent. Suitable solvents include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene and xylene. Suitable solvents also include
55 liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene and vinyltoluene (including all isomers alone or in admixture).

It is believed that the active catalyst species of the present invention contains a metal center which center remains cationic, unsaturated and has a metal-carbon bond which is reactive with olefins, diolefins and acetylenically unsaturated compounds. Also associated with this metal center is a charge balancing anionic remnant of the formula A⁻.

The catalyst formed by the method of this invention may be retained in solution or separated from the solvent, isolated, and stored for subsequent use. As previously indicated supra, the catalyst may also be prepared *in situ* during a polymerization reaction by passing the separate components into the polymerization vessel where the components will contact and react to produce the improved catalyst of this invention.

The equivalent ratio of derivative of a Group 4, or Lanthanide metal compound to oxidizing agent compound employed is preferably in a range from 0.1:1 to 10:1, more preferably from 0.75:1 to 2:1, most preferably 1.0:1.0. In most polymerization reactions the equivalent ratio of catalyst:polymerizable compound employed is from 10⁻¹²:1 to 10⁻¹:1, more preferably from 10⁻⁶:1 to 10⁻³:1.

A beneficial feature of some of the catalysts of this invention, particularly those based on monocylopentadienyl substituted titanium compounds in combination with an oxidizing agent comprising boron, is that when the catalysts of this invention are used to copolymerize α -olefins, either alone or in combination with diolefins, the amount of higher molecular weight olefin or diolefin incorporated into the copolymer is significantly increased when compared to copolymers prepared with the more conventional Ziegler-Natta type catalysts. The relative rates of reaction of ethylene and higher α -olefins with the aforementioned titanium-based catalysts of this invention are so similar that the monomer distribution in copolymers prepared with the catalysts of this invention may be controlled by the ratio of monomeric reactants.

"Addition polymerizable monomers" usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, acetylenic compounds and conjugated or nonconjugated dienes. Preferred monomers include the C₂₋₁₀ α -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, and 1,4-hexadiene.

In general, catalysts can be selected so as to produce polymer products which will be free of certain trace impurities such as aluminum, magnesium and chloride generally found in polymers produced with Ziegler-Natta type catalysts. The polymer products produced with the catalysts of this invention should, then, have a broader range of applications than polymers produced with more conventional Ziegler-Natta type catalysts comprising a metal alkyl such as an aluminum alkyl.

Having described the invention the following examples are provided as further illustration thereof. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

Example 1

To 25 ml of deaerated purified toluene, 25 micromoles of (tert-butylamido)dimethyl(η^5 -cyclopentadienyl)silanedibenzylzirconium and 25 micromoles of ferrocenium perfluorotetraphenyl borate were added. The mixture was agitated for approximately 1 minute until the blue color of the solid ferrocenium salt was discharged.

Polymerization

A 4 L reactor was charged with 2 L of mixed alkane solvent (Isopar ETM) and 300 ml of 1-octene, heated to 150°C and pressurized with ethylene to 31 atmospheres (3.1 MPa). All components had been previously deaerated and purified. 20 ml of the above catalyst solution were added resulting in an immediate rapid uptake of ethylene and a large rise in reactor temperature (approximately 50 g per minute ethylene uptake and temperature rise of 26°C). At the end of a 10 minute period the reactor contents were removed and devolatilized leaving 78 g of ethylene/1-octene copolymer. The 1-octene content of the polymer was 7.5 mole percent as determined by mass balance.

Example 2

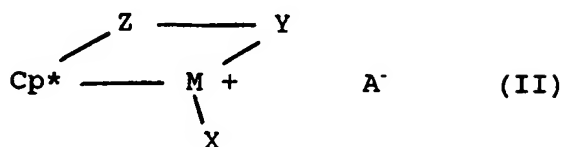
A catalyst solution was prepared by mixing 10 micromoles each of (tert-butylamido)dimethyl(η^5 -2,3,4,5-tetramethylcyclopentadienyl)silane dibenzyl titanium and ferrocenium perfluorotetraphenylborate in 5 milliliters of toluene. After thirty seconds of agitation the blue ferrocenium had been consumed and a greenish brown solution formed.

Polymerization

Addition of this catalyst solution to a stirred (500 rpm) two liter reactor containing Isopar-ETM (1000 ml), 1-octene (200 ml), hydrogen (50 ml at 50 psi, 350 kPa) and ethylene (saturated at 450 psi, 3 MPa) at 130°C resulted in a 40°C temperature rise. Ten minutes after addition of the catalyst solution to the reactor the contents were removed from the reactor and the volatiles stripped to give 104 g of linear low density polyethylene.

Claims

1. A process for preparing an addition polymerization catalyst of the formula (II):



wherein:-

M is a metal of Group 4 or the Lanthanide series of the periodic Table of the Elements;

X is hydride or a hydrocarbyl, silyl or germyl group having up to 20 carbon, silicon or germanium atoms;

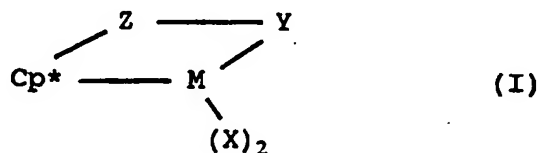
Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound to Z and bound in an η^5 bonding mode to M, said substituents being independently selected from hydrocarbyl radicals, substituted-hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by halogen atoms, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, or halogen radicals or two or more such substituents together form a fused ring system;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system; and

A⁻ is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom selected from aluminum, gold, platinum, boron, phosphorus and silicon,

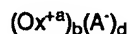
comprising contacting a derivative of a Group 4 or Lanthanide metal corresponding to the formula (I):



wherein:-

M, X, Cp*, Z and Y are as defined above

with an oxidizing agent which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent corresponding to the formula:



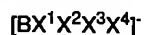
wherein:-

Ox^{+a} is a non-Bronsted acid, cationic oxidizer having a charge of (+a) selected from ferrocenium ions, bis-indenyl Fe(III) ions, cationic derivatives of substituted ferrocene, Ag⁺¹, Pd⁺², Pt⁺², Hg⁺², Hg₂⁺², Au⁺ and Cu⁺;

A⁻ is as previously defined; and

b and d are integers selected to provide charge balance.

2. A process as claimed in Claim 1, wherein M is titanium or zirconium.
3. A process as claimed in Claim 2, wherein each X independently is hydride, trimethylsilyl, or a moiety selected from alkyl, aryl and combinations thereof of up to 10 carbon atoms; Y is NR'; and Z is (ER'₂)_m, wherein each R' independently is hydrogen, silyl, alkyl, aryl or a combination thereof having up to 10 carbon or silicon atoms or two R' together with the cyclopentadienyl group form an indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl ring; E is carbon or silicon; and m is 1 or 2.
4. A process as claimed in Claim 3, wherein E is silicon.
5. A process as claimed in any one of the preceding claims, wherein the cationic oxidizer has an oxidation potential of at least +0.20 volt.
6. A process as claimed in Claim 5, wherein the cationic oxidizer has an oxidation potential is at least +0.25 volt.
7. A process as claimed in any one of the preceding claims, wherein Ox^{+a} is ferrocenium or Ag⁺¹.
8. A process as claimed in any one of the preceding claims, wherein A⁻ is:



wherein:

B is boron in a valence state of 3 and

X¹ to X⁴ are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms and optionally two or more of X¹ to X⁴ may be linked to each other through a stable bridging group.

9. A process as claimed in Claim 8, wherein X¹, X², X³, and X⁴ are selected from perfluorinated hydrocarbyl radicals containing from 6 to 20 carbons, 3,4,5-trifluorophenyl and 3,5-bis(trifluoromethyl)phenyl.
10. A process as claimed in Claim 9, wherein A⁻ is tetrakis(pentafluorophenyl) borate.
11. A process as claimed in any one of the preceding claims, wherein X is hydride or C₁-C₁₀ hydrocarbyl.
12. A process as claimed in Claim 11, wherein X is benzyl.
13. A process as claimed in Claim 11, wherein X is methyl.
14. A process as claimed in any one of Claims 1 to 13, wherein Cp* is unsubstituted cyclopentadienyl or tetramethylcyclopentadienyl.
15. An addition polymerization catalyst of Formula II as defined in Claim 1, said catalyst lacking in amine or phosphine byproducts and being obtainable by the process as claimed in Claim 1.
16. A catalyst as claimed in Claim 15, wherein M, X, Y, Z and A⁻ are as defined in any one of Claims 2, 3, 4 and 8 to 13.
17. A catalyst as claimed in Claims 15 or Claim 16, wherein Cp* is unsubstituted cyclopentadienyl or tetramethylcyclopentadienyl.
18. The use as an addition polymerization catalyst of a catalyst as claimed in any one of Claims 15 to 17 or obtained by a process as claimed in any one of Claims 1 to 14.
19. A use as claimed in Claim 18, wherein the catalyst is formed *in situ*.

20. A use as claimed in Claim 18, wherein the catalyst is used in a solvent in which it is prepared by a process of Claim 1.

21. A use as claimed in Claim 18, wherein the catalyst is a direct (i.e. unpurified) product of a process of Claim 1.

22. A catalytic addition polymerization process characterized in that the catalyst is as claimed in any one of Claims 15 to 17 or obtained by a process as claimed in any one of Claims 1 to 14.

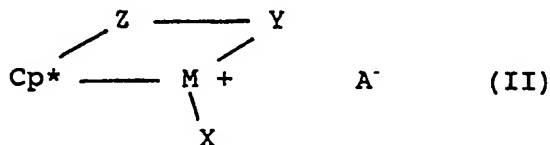
23. A process as claimed in Claim 22, wherein the catalyst is formed in situ.

24. A process as claimed in Claim 22, wherein the catalyst is used in a solvent in which it is prepared by a process of Claim 1.

25. A process as claimed in Claim 22, wherein the catalyst is a direct (i.e unpurified) product of a process of Claim 1.

Patentansprüche

1. Verfahren zur Herstellung eines Additionspolymerisationskatalysators der Formel (II)



worin

M ein Metall der Gruppe 4 oder der Lanthanidreihe des Periodensystems der Elemente ist,

X Hydrid oder eine Kohlenwasserstoff-, Silyl- oder Germylgruppe mit bis zu 20 Kohlenstoff-, Silicium- oder Germaniumatomen ist,

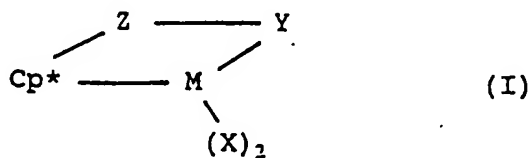
Cp* eine Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe ist, die an Z gebunden ist und mit einer η^5 -Bindung an M gebunden ist, wobei diese Substituenten unabhängig voneinander ausgewählt sind aus Kohlenwasserstoffresten, substituierten Kohlenwasserstoffresten, worin ein oder mehrere Wasserstoffatome durch Halogenatome ersetzt sind, kohlenwasserstoffsubstituierten Metalloidresten, worin das Metalloid ausgewählt ist aus der Gruppe 14 des Periodensystems der Elemente, oder Halogenresten oder zwei oder mehreren solcher Substituenten, die zusammen ein kondensiertes Ringsystem bilden,

Z eine zweiwertige Einheit ist, die Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente enthält,

Y eine verbindende Gruppe ist, die Stickstoff, Phosphor, Sauerstoff oder Schwefel enthält, oder wahlweise Z und Y zusammen ein kondensiertes Ringsystem bilden, und

A⁻ ein einfacher Koordinationskomplex ist, der eine Vielzahl von lipophilen Resten enthält, die kovalent an ein zentrales, formal ladungstragendes Metall- oder Metalloidatom, ausgewählt aus Aluminium, Gold, Platin, Bor, Phosphor und Silicium, koordiniert sind und dieses abschirmen,

durch Inkontaktbringen eines Derivats eines Gruppe-4- oder Lanthanidmetalls entsprechend der Formel (I)



worin

M, X, Cp*, Z und Y wie oben definiert sind,

mit einem Oxidationsmittel, das in reduzierter Form nicht mit dem resultierenden Katalysator wechselwirkt, wobei dieses Oxidationsmittel der Formel $(Ox^{+a})_b(A^-)_d$ entspricht, worin

Ox^{+a} ein kationisches Oxidationsmittel mit einer Ladung von $(+a)$, ausgewählt aus Ferroceniumionen, Bisindenyl-Fe(III)-Ionen, kationischen Derivaten eines substituierten Ferrocens, Ag^{+1} , Pd^{+2} , Pt^{+2} , Hg^{+2} , Hg_2^{+2} , Au^{+} und Cu^{+} , ist, das keine Brönsted-Säure ist,

A^- wie vorhergehend beschrieben definiert ist und

b und d ganze Zahlen sind, die so ausgewählt sind, daß Ladungsneutralität gegeben ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß M Titan oder Zirkon ist.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet,

daß jedes X unabhängig voneinander Hydrid, Trimethylsilyl oder eine Einheit, ausgewählt aus Alkyl, Aryl und Kombinationen davon mit bis zu 10 Kohlenstoffatomen, ist, Y NR' ist und Z $(ER'_2)_m$ ist, worin jedes R' unabhängig voneinander Wasserstoff, Silyl, Alkyl, Aryl oder eine Kombination davon mit bis zu 10 Kohlenstoff- oder Siliciumatomen ist oder zwei R' zusammen mit der Cyclopentadienylgruppe einen Indenyl-, Tetrahydroindenyl-, Fluorenyl- oder Octahydrofluorenylring ausbilden, E Kohlenstoff oder Silicium ist und m 1 oder 2 ist.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß E Silicium ist.

5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das kationische Oxidationsmittel ein Oxidationspotential von wenigstens +0,20 V hat.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das kationische Oxidationsmittel ein Oxidationspotential von wenigstens +0,25 V hat.

7. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß Ox^{+a} Ferrocenium oder Ag^{+1} ist.

8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß $A^- [BX^1X^2X^3X^4]^-$ ist, worin

B Bor ist in einem Valenzzustand von 3 und

X^1 bis X^4 gleiche oder unterschiedliche, nichtreaktive, organische oder Silylreste mit 6 bis 20 Kohlenstoffatomen oder Siliciumatomen sind und wahlweise zwei oder mehrere der X^1 bis X^4 miteinander über eine stabile Verbrückungsgruppe verbunden sind.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet,

daß X^1 , X^2 , X^3 und X^4 ausgewählt sind aus perfluorierten Kohlenwasserstoffresten mit 6 bis 20 Kohlenstoffatomen, 3,4,5-Trifluorphenyl und 3,5-Bis(trifluormethyl)phenyl.

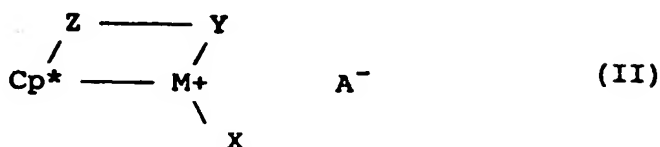
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß A^- Tetrakis(pentafluorphenyl)borat ist.

11. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß X Hydrid oder eine C_1 - C_{10} -Kohlenwasserstoffgruppe ist.

12. Verfahren nach Anspruch 11,
dadurch gekennzeichnet,
daß X Benzyl ist.
- 5 13. Verfahren nach Anspruch 11,
dadurch gekennzeichnet,
daß X Methyl ist.
- 10 14. Verfahren nach einem der Ansprüche 1 bis 13,
dadurch gekennzeichnet,
daß Cp* nichtsubstituiertes Cyclopentadienyl oder Tetramethylcyclopentadienyl ist.
- 15 15. Additionspolymerisationskatalysator der Formel II, wie in Anspruch 1 definiert, wobei dieser Katalysator nicht zu
Amin- oder Phosphin Nebenprodukten führt und erhältlich ist durch das Verfahren nach Anspruch 1.
16. Katalysator nach Anspruch 15,
dadurch gekennzeichnet,
daß M, X, Y, Z und A⁻ so sind, wie in einem der Ansprüche 2, 3, 4 und 8 bis 13 definiert.
- 20 17. Katalysator nach Anspruch 15 oder 16,
dadurch gekennzeichnet,
daß Cp* nichtsubstituiertes Cyclopentadienyl oder Tetramethylcyclopentadienyl ist.
- 25 18. Verwendung eines Katalysators nach einem der Ansprüche 15 bis 17 oder erhalten durch ein Verfahren nach
einem der Ansprüche 1 bis 14 als Additionspolymerisationskatalysator.
19. Verwendung nach Anspruch 18,
dadurch gekennzeichnet,
daß der Katalysator in situ gebildet wird.
- 30 20. Verwendung nach Anspruch 18,
dadurch gekennzeichnet,
daß der Katalysator in einem Lösungsmittel verwendet wird, in dem er durch ein Verfahren nach Anspruch 1 her-
gestellt worden ist.
- 35 21. Verwendung nach Anspruch 18,
dadurch gekennzeichnet,
daß der Katalysator ein direktes (d.h. ungereinigtes) Produkt des Verfahrens nach Anspruch 1 ist.
- 40 22. Katalytisches Additionspolymerisationsverfahren,
dadurch gekennzeichnet,
daß der Katalysator so ist, wie in einem der Ansprüche 15 bis 17 beansprucht, oder erhalten wird nach einem Ver-
fahren, wie es in einem der Ansprüche 1 bis 14 beansprucht ist.
- 45 23. Ein Verfahren nach Anspruch 22,
dadurch gekennzeichnet,
daß der Katalysator in situ gebildet wird.
- 50 24. Ein Verfahren nach Anspruch 22,
dadurch gekennzeichnet,
daß der Katalysator in einem Lösungsmittel verwendet wird, in dem er durch ein Verfahren nach Anspruch 1 her-
gestellt worden ist.
- 55 25. Ein Verfahren nach Anspruch 22,
dadurch gekennzeichnet,
daß der Katalysator ein direktes (d.h. ungereinigtes) Produkt des Verfahrens nach Anspruch 1 ist.

Revendications

1. Procédé pour préparer un catalyseur de polymérisation d'addition de formule (II):



dans laquelle:

M est un métal du groupe 4 ou de la série des lanthanides du Tableau Périodique des Eléments;
 X est un hydruure ou un groupe hydrocarbyle, silyle ou germyle ayant jusqu'à 20 atomes de carbone, de silicium ou de germanium;

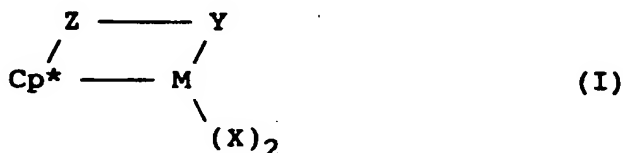
Cp* est un groupe cyclopentadiényle ou cyclopentadiényle substitué lié à Z et lié par un mode de liaison η^5 à M, lesdits substituants étant indépendamment choisis parmi les radicaux hydrocarbyle, les radicaux hydrocarbyle substitués dans lesquels un ou plusieurs atomes d'hydrogène sont remplacés par des atomes d'halogène, les radicaux hydrocarbyle substitués métalloïdes dans lesquels le métalloïde est choisi dans le Groupe 14 du Tableau Périodique des Eléments, ou les radicaux halogène ou deux ou plus de ces substituants forment ensemble un système de noyau condensé;

Z est un radical divalent comprenant l'oxygène, le bore ou un élément du Groupe 14 du Tableau Périodique des Eléments;

Y est un groupe de liaison comprenant l'azote, le phosphore, l'oxygène ou le soufre ou éventuellement Z et Y forment ensemble un système de noyau condensé; et

A est un complexe de coordination simple comprenant un ensemble de radicaux lipophiles coordonnés de façon covalente et masquant un atome de métal ou un atome de métalloïde central portant formellement une charge, choisi parmi l'aluminium, l'or, le platine, le bore, le phosphore et le silicium,

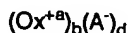
consistant à mettre en contact un dérivé d'un métal du Groupe 4 ou des lanthanides correspondant à la formule (I):



dans laquelle:

M, X, Cp*, Z et Y sont tels que définis ci-dessus

avec un agent oxydant qui sous forme réduite n'interfère pas avec le catalyseur obtenu, ledit agent oxydant correspondant à la formule:



dans laquelle:

Ox^{+a} est un oxydant cationique qui n'est pas un acide de Bronsted ayant une charge (+a), choisi parmi les ions ferrocénium, les ions bis-indényle Fe(III), les dérivés cationiques de ferrocène substitué, Ag^{+1} , Pd^{+2} , Pt^{+2} , Hg^{+2} , Hg_2^{+2} , Au^+ et Cu^+ ;

A^- est tel que défini précédemment; et

b et d sont des nombres entiers choisis de façon à fournir un équilibre des charges.

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2. Procédé selon la revendication 1, dans lequel M est le titane ou le zirconium.
3. Procédé selon la revendication 2, dans lequel chaque X est indépendamment un hydruure, le triméthylsilyle, ou un radical choisi parmi les groupes alkyle, aryle ou leurs combinaisons ayant jusqu'à 10 atomes de carbone; Y est NR'; et Z est (ER')₂, chaque R' étant indépendamment un atome d'hydrogène, un groupe silyle, alkyle, aryle ou une de leurs combinaisons ayant jusqu'à 10 atomes de carbone ou de silicium ou deux R' forment avec le groupe cyclopentadiényle un noyau indényle, tétrahydroindényle, fluorényle ou octahydrofluorényle; E est un atome de carbone ou de silicium; et m vaut 1 ou 2.
4. Procédé selon la revendication 3, dans lequel E est la silice.
5. Procédé selon l'une des revendications précédentes, dans lequel l'oxydant cationique a un potentiel d'oxydation d'au moins +0,20 volt.
6. Procédé selon la revendication 5, dans lequel l'oxydant cationique a un potentiel d'oxydation d'au moins +0,25 volt.
7. Procédé selon l'une des revendications précédentes, dans lequel Ox^{+a} est le ferrocénium ou Ag⁺¹.
8. Procédé selon l'une des revendications précédentes, dans lequel A⁻ est:

$$[BX^1X^2X^3X^4]^-$$
 dans laquelle:
 B est un atome de bore à l'état de valence 3;
 X¹ à X⁴ sont les radicaux organyle ou silyle non réactifs, identiques ou différents contenant de 6 à 20 atomes de carbone ou de silicium et éventuellement deux radicaux ou plus parmi X¹ à X⁴ peuvent être liés l'un à l'autre grâce à un groupe de pontage stable.
9. Procédé selon la revendication 8, dans lequel X¹, X², X³ et X⁴ sont choisis parmi les radicaux hydrocarbyle perfluorés contenant de 6 à 20 atomes de carbone, le 3,4,5-trifluorophényle et le 3,5-bis(trifluorométhyl)phényle.
10. Procédé selon la revendication 9, dans lequel A⁻ est le tétrakis(pentafluorophényle)borate.
11. Procédé selon l'une des revendications précédentes, dans lequel X est un hydruure ou un hydrocarbyle en C₁ à C₁₀.
12. Procédé selon la revendication 11, dans lequel X est le benzyle.
13. Procédé selon la revendication 11, dans lequel X est le méthyle.
14. Procédé selon l'une des revendications 1 à 13, dans lequel Cp* est un cyclopentadiényl non substitué ou un tétraméthylcyclopentadiényle.
15. Catalyseur de polymérisation par addition de formule II tel que défini dans la revendication 1, ledit catalyseur étant dépourvu d'amine ou de phosphine comme sous-produits et étant susceptible d'être obtenu par le procédé de la revendication 1.
16. Catalyseur selon la revendication 15, dans lequel M, X, Y, Z et A⁻ sont tels que définis dans l'une des revendications 2, 3, 4 et 8 à 13.
17. Catalyseur selon l'une des revendications 15 ou 16, dans lequel Cp* est un cyclopentadiényle non substitué ou un tétraméthylcyclopentadiényle.
18. Utilisation comme catalyseur de polymérisation par addition d'un catalyseur tel que revendiqué dans l'une des revendications 15 ou 17 ou obtenu par un procédé selon l'une des revendications 1 à 14.
19. Utilisation selon la revendication 18, selon laquelle le catalyseur est formé in situ.

20. Utilisation selon la revendication 18, selon laquelle le catalyseur est utilisé dans le solvant dans lequel il a été préparé selon le procédé de la revendication 1.

21. Utilisation selon la revendication 18, selon laquelle le catalyseur est un produit direct (non purifié) du procédé de la revendication 1.

22. Procédé catalytique de polymérisation par addition, caractérisé par le fait que le catalyseur est celui revendiqué dans l'une des revendications 15 à 17 ou obtenu par le procédé de l'une des revendications 1 à 14.

23. Procédé selon la revendication 22, dans lequel le catalyseur est formé in situ.

24. Procédé selon la revendication 22, dans lequel le catalyseur est utilisé dans le solvant dans lequel il a été préparé par le procédé de la revendication 1.

25. Procédé selon la revendication 22, dans lequel le catalyseur est un produit direct (non purifié) du procédé de la revendication 1.

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